Surface Tension Measurement of Molten Metal using A Falling Droplet in A Short Drop Tube†

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Abstract

A drop tube-type short time microgravity system was developed to measure the surface tension of high temperature melts using an oscillating drop method. The oscillation of a falling droplet was precisely recorded using the combination of a line sensor and a laser backlight. The surface oscillation of the droplet was quite simple during the falling, and consequently, the surface tension was calculated using Rayleigh's equation. The measurements were carried out over a wide temperature range including the undercooling state. The obtained surface tension of copper is expressed as below.

$\gamma = 1257 - 0.20\ (T - 1356)$ (mN/m) (T: 1287K-1998K)

KEY WORDS: (Microgravity) (Surface tension) (Drop tube) (Oscillating drop method)

1. Introduction

The Marangoni flow has a large effect on the weld shape[1,2], because the shape depends on the convection inside the welding pool. Although the convection depends on the balance among several forces such as the Marangoni force, the electromagnetic force, the air drag force and the buoyancy, the Marangoni flow can often be the main factor. For example, when welding is conducted for stainless steels, the depth of the weld pool is smaller for a low sulfur content, but it is larger for a high sulfur content[3-5]. It is considered that the change in the direction of the Marangoni flow on the pool surface causes this phenomenon.

In order to calculate the shape of the weld pool using a numerical simulation, all of the above-mentioned forces are included and suitable physical properties are necessary[4,6]. However, it is very difficult to obtain precise surface tension data because the surface tension is affected by very small amounts of contamination. When the surface tension of the molten metal is measured by a traditional sessile drop method, the sample reacts with a substrate and the composition of the sample differs from original one after the measurement. This tendency is stronger for higher temperatures.

The oscillating drop method is very suitable for the measurement of high temperature melts because it is a container-less measurement method. The purity of the sample is maintained during the measurement because no reaction occurs between the sample and the crucible even at high temperature. In addition, an undercooling state is easily achieved when using this method. Thus, the measurements can be carried out over a much wider temperature range. Furthermore, the density value of the sample is not required for the oscillating drop method. When other measurement methods are used, differences in the adopted density values produce different calculated surface tension values. In the oscillating drop method, the surface tension value is calculated from the droplet mass and the frequency of the oscillation. These variables are easily measured with high accuracy. Consequently, the accuracy of this method is much higher. The theory of the surface oscillation was investigated by Rayleigh[7] and Lamb[8]. Fraser et al. first applied the electromagnetic technique to the surface tension measurement at high temperatures[9], and since then many researchers have used this technique.

Although this method has many advantages, there is one disadvantage. When the measurement is carried out under terrestrial conditions, a strong lifting force against gravity is necessary, and this force affects the surface oscillation. As a result, several oscillations with different frequencies exist at the same time[10], and consequently, it

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is impossible to determine the precise surface tension using Rayleigh's theory. For this problem, correction formulae have been proposed[11,12]. However, when such formulae are adopted, the high accuracy and the simplicity of the measurement principle are lost. Another approach to obtain a precise surface tension value is to use microgravity conditions. Under microgravity, no lifting force is necessary and the surface oscillation can be very simple. Egry et al. measured many kinds of thermophysical properties, such as the surface tension, density, viscosity, and electric conductivity, under microgravity[13]. The obtained surface tension values were compared with the values obtained at 1G in order to confirm the reliability of the correction formula[14]. Fujii et al. also measured the surface tension under microgravity[15, 16]. They precisely investigated the surface oscillation of a droplet and showed the effect of the shape deformation on the obtained surface tension values[17].

As already mentioned before, microgravity utilization is an effective way to obtain ideal experimental conditions. On the other hand, many restrictions are imposed on the cost, the schedule, and the experimental apparatus. In order to use microgravity conditions more conveniently, our group constructed a 1.4m drop-tube to carry out the measurements of the surface tension and viscosity of a water droplet[18]. The oscillating drop method was used for a falling droplet. A simple surface oscillation was obtained under the microgravity conditions and the surface tension and the viscosity of water were calculated without any correction formulae.

In this study, the short drop tube was improved for the measurement at high temperatures and the surface tension of pure molten copper was measured. The sample was levitated and melted using an electromagnetic levitation method. The falling was started by turning off the levitation force and the surface oscillation of the droplet was recorded during the short falling period of 0.5 sec. The surface tension was calculated from the recorded oscillation data using Rayleigh's equation without any correction formula

2. Principle

The surface tension is described as a function of the frequency of the surface oscillation by eq.1 [7],

$$\gamma = \frac{3}{8}\pi M\omega^2, \qquad (1)$$

where γ is the surface tension, M is the mass of a droplet and ω is the frequency of the surface oscillation. When a droplet is levitated using the electromagnetic levitation method, the surface oscillation of the droplet consists of several oscillations of different frequencies. In addition, the frequencies shift to higher values due to the effect of the electromagnetic field. In such a case, the surface tension cannot be calculated using above equation.

3. Experimental

3.1 Apparatus

A schematic diagram of the measurement system is shown in **Fig. 1**. The system is equipped with a drop tube, a coil, a radio frequency generator, two line sensors, and a UV pyrometer. The silica drop tube is 1.3m long with a 15mm outer diameter. This drop tube is positioned inside a furnace in order to maintain the temperature of the falling sample. The temperature distribution of the furnace is adjusted using three heaters that are controlled independently. The levitation coil is wound from a 3mm outer diameter copper tube and the radio frequency generator can supply a 20kW AC current at 300kHz for the coil. The oscillation of the droplet is measured using combination of a laser back light, two cylindrical lenses, and two line sensors. Because the droplet falls inside the laser column, the shadow of the droplet is always projected onto the line sensors during its fall. The cylindrical lenses focus the shadow of the droplet in one direction so that the shadow should be observed as a dark line on the line sensors, as shown in **Fig. 2**. As a result, the maximum length of the droplet in one direction is measured. In order to determine the oscillation frequency with high accuracy, a sufficient number of oscillation cycles should be counted during the falling period. Accordingly, a 0.05g sample was used because the

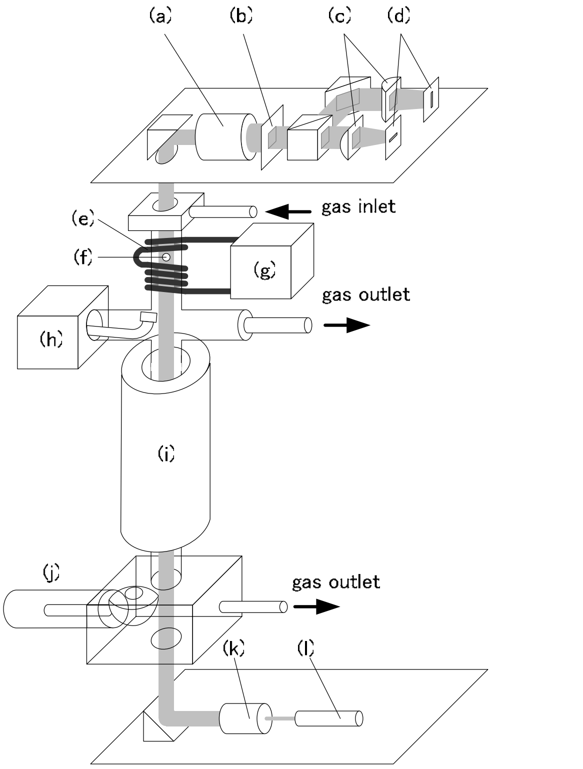

Fig. 1 Schematic diagram of the measurement system for the oscillating drop method.
(a)Beam expander, (b)Slit, (c)Cylindrical lens, (d)Line sensors, (e)Coil, (f)Sample, (g)RF Generator, (h)Sample stage, (i)heater, (j)mold, (k)Beam expander, (l)He-Ne laser

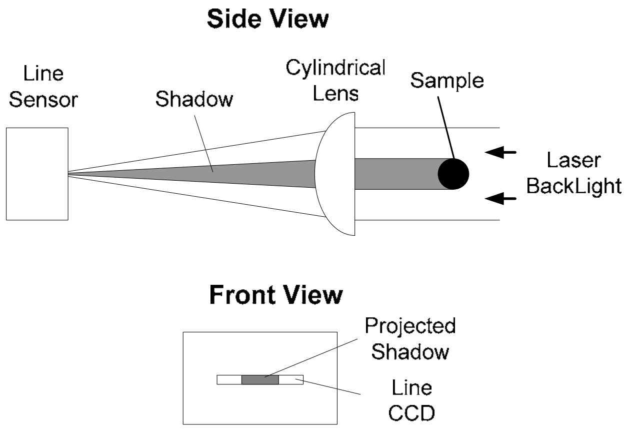

Fig. 2 Projection of a droplet shadow.

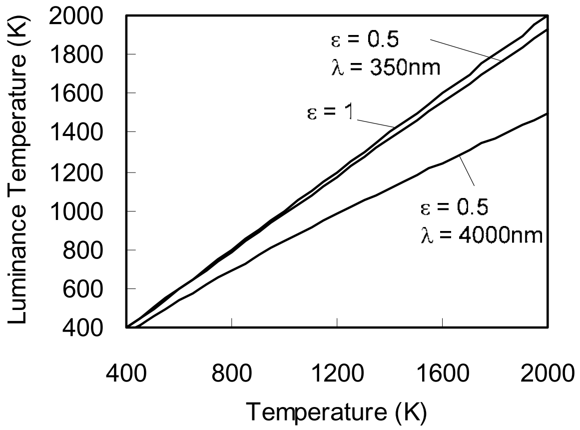

Fig. 3 Relationship between temperature and luminance temperature.

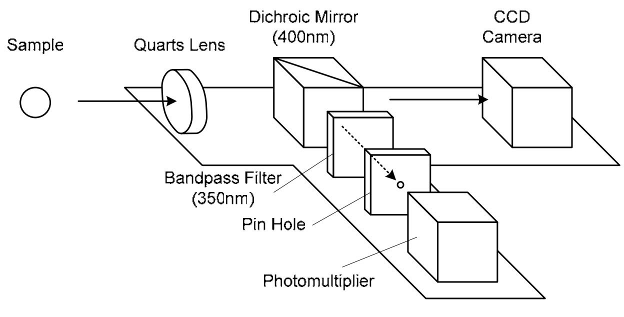

Fig. 4 Schematic diagram of the UV pyrometer.

resonance frequency is higher for a smaller droplet. A line sensor is suitable for measuring such a small and fast oscillation because a faster recording rate with more pixels can be recorded for one line than for an area CCD. The line sensors used in this study can record 2048 pixels in one line at 84000 line/sec. At the end of the fall, a copper mold moves into the center from the side of the tube to capture the droplet. The weight of the sample was determined from the captured sample.

3.2 Temperature Measurement

A newly developed pyrometer detecting ultraviolet rays was used to measure the sample temperature. Radiation thermometry is usually adopted when any contact with other objects should be avoided. However, a noticeable error is usually included in the result when the accurate emissivity of the object is not available. According to Planck's law of radiation, the effect of temperature on the spectral radiance is greater at shorter wavelengths. Namely, the effect of the emissivity is lower when a shorter wavelength is adopted for the radiation thermometry[19-22]. **Figure 3** shows the relationship between the actual temperature and the luminous temperature when the wavelength is 350nm and 4000nm. The effect of the emissivity is lower for the wavelength of 350nm.

A schematic diagram of the pyrometer is shown in **Fig. 4**. A dichroic mirror selectively reflects an incident ray with wavelengths shorter than 400nm. The rays with wavelengths longer than 400nm pass through the dichroic mirror and reach the CCD camera in order to determine the measurement position and adjust the focus. After the transmission through a band-pass filter with the center wavelength of 350nm, the ray is focused on a pinhole in order to define the measurement area. Pinholes with diameters of 0.4mm or 1.0mm were used in this study. The 0.4mm diameter was selected for use at the higher temperatures and the 1.0mm diameter was selected for the lower temperatures. The intensity of the ray was measured by a photomultiplier. The pyrometer was calibrated by measuring the radiation of a carbon cavity in a temperature-controlled furnace. In addition, the effective emissivity was calibrated using the melting point of a levitating copper droplet in order to remove the effect of the difference in the optical characteristics between the levitation furnace and the temperature-controlled furnace.

3.3 Experimental Conditions

The sample was cut from a 99.999% Cu wire, cleaned in dilute nitric acid to remove any surface oxide, rinsed in water, and then washed in acetone. After the drop-tube was evacuated, a mixture of Ar-3%H_2 and He-3%H_2, both of which were purified by a moisture reducer, an oxygen absorber, dry ice and a magnesium getter. The oxygen partial pressure of the gas was measured at 1273K at the inlet of the drop-tube using a calcia-stabilized zirconia sensor with reference to the oxygen partial pressure of the Si-SiO_2 equilibrium. In this study, an unstable electromotive force was observed due to the higher electron conductivity at temperatures higher than 1273K. Because electron conductivity of the calcia-stabilized zirconia is generally high under very low oxygen partial pressure conditions[23], it is impossible to obtain the absolute value of the oxygen partial pressure. However, we did determine that the oxygen partial pressure is lower than the reference oxygen partial pressure of 10^{-28} atm.

After the sample was levitated and melted by the electromagnetic levitation method, the sample temperature was increased to approximately 2073K in order to remove the oxide film on the sample surface. When the temperature and the motion of the sample reached the requisite values, then the droplet was allowed to drop by turning off the coil current. Because the collected sample is too small for an oxygen analysis, a larger sample weighing 0.3g was processed with the same sequence and solidified under the levitating conditions. The oxygen content was measured by the non-dispersible infrared absorption method and the value of 1ppm was obtained for the processed sample and 3ppm was obtained for the original material.

4. Results and Discussion

Frequency spectrums of the surface oscillation before and during falling are shown in **Fig. 5**. The several peaks in the spectrum mean that there are several oscillations with different frequencies under the terrestrial conditions. A single peak is obtained in 0.05 sec after the start of falling. This result indicates that no external force acts on the falling droplet.

The calculated surface tension values are shown along with the previous values[24-30] in **Fig. 6**. Measurements were carried out in the wide temperature range from 1287K to 1998K, which includes undercooling states. The surface tension of molten copper is represented as follows:

$$\gamma = 1257 - 0.20\,(T - 1356) \quad \text{(mN/m)}$$
$$(T\text{: 1287K-1998K})$$

Generally speaking, it is considered that higher surface tension values are obtained under purified conditions[25] because even a small amount of contamination or impurity decreases the surface tension. In particular, the surface tension of copper is easily decreased by oxygen [24,29,30]. In order to use the measured values, the amount of oxygen on the surface should be known. Unfortunately, it is impossible to measure the amount of adsorbed oxygen on the surface. Also, the oxygen content in the sample is difficult to measure precisely when the amount is very small. Therefore, the oxygen partial pressure is usually measured and the oxygen content is assumed to reach equilibrium[29]. In order to check whether the equilibrium is reached or not, the measurement was carried out using a sample which was allowed to levitate at 1373K for three hours. As a result, the obtained surface tension value was found to be the same as the other sample with a short levitation time. Therefore, the oxygen content in the sample is considered to reach equilibrium.

The resolution of the measured frequency is 5Hz. The error in the surface tension value caused by this resolution is estimated to be ±4%. This estimation has good agreement with the scattering of the measured surface tension values. The relative resolution to the resonance frequency of the droplet can be improved by reducing the droplet size. In this study, a sample with the

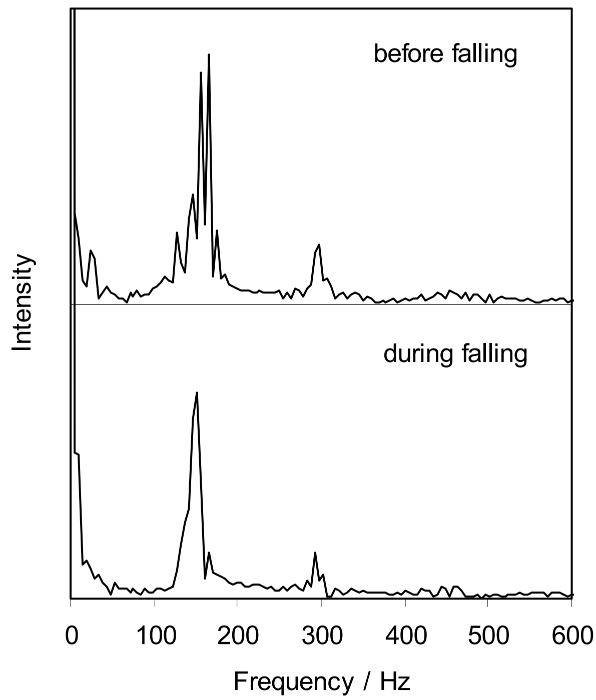

Fig. 5 Frequency spectrum of the oscillation before and during falling.

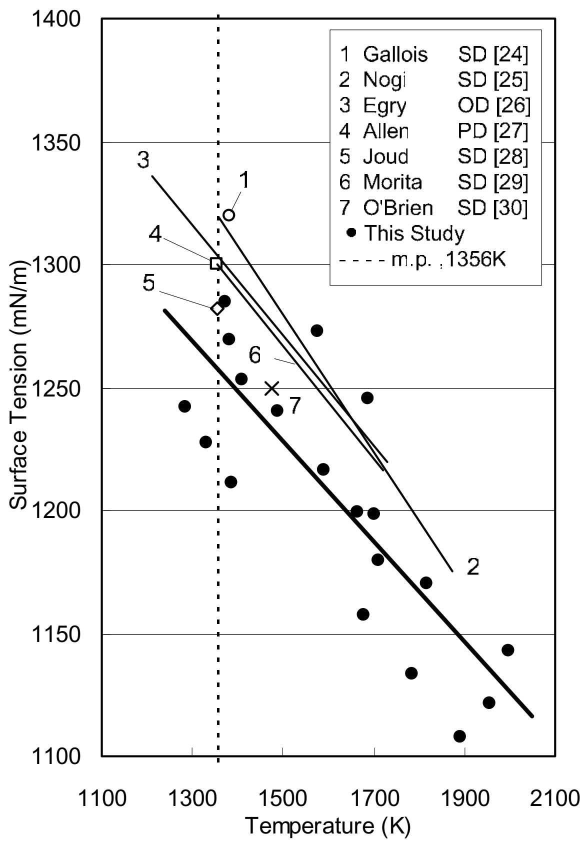

Fig. 6 Surface tension of molten copper.
OD: Oscillating Drop Method, SD: Sessile Drop Method, PD Pendant Drop Method

diameter of 2.2 mm is used and the resonant frequency of 140Hz is obtained. When a 1.0mm sample is used, the resonance frequency is estimated to be 470Hz and the error in the measured surface tension will be decreased to ±1%.

5. Conclusions

The surface tension of molten copper was measured by the free-fall oscillating drop method. The surface oscillation of the droplet was quite simplified while falling and the surface tensions were calculated using Rayleigh's equation. The obtained surface tension of copper is expressed as follows:

$\gamma = 1257 - 0.20\,(T - 1356)$ (mN/m)
(T: 1287K-1998K)

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